

For nuclides of the second group for practically full disintegration (the decrease of activity in 100 000 times) it is necessary time about 500 years.

Nuclides of the third group for their disintegration need time measured in millions of years that far leaves the frameworks of the most optimistic estimations of durability of the cured mixtures on the base of portland cement.

Outgoing from above-stated, is reasonable to esteem cementation with mixtures on the basis of portland cement as reasonable method for maintenance of safe storage of the radwastes containing nuclides of the first and the second groups for it is necessary that the durability of mixtures was not less than 500 years. Apparently, that for estimation of suitability cement mixtures for this purpose it is desirable to have possibility to predict their durability in conditions of affect on them of gamma-radiation and storage environment.

The analysis of reasons which can lead to decrease of strength and impairment of other physicochemical properties of concretes has shown that *the primary one is the* interaction with groundwater and temperature regime of storage. The negative influencing on durability of concrete can be done also by irradiation, but this factor can become essential only for objects with high level of radiation (absorbed dose more than 2000 Mrad).

Interaction with groundwater leads to leaching from concrete dissoluble calcium compounds that results in change of structure of solid phases of cement matrix and, as consequent of it, to decrease of strength and change of other physicochemical properties of concrete. Besides the contact with groundwater is a reason of leaching of radionuclides from cement matrixes.

The negative influencing on durability of concrete can render also periodic cooling it up to temperature at which freezing a liquid in pores of cement matrix can take place that can lead to development of microcracks in structure of concrete that results in decrease of its strength, acceleration of leaching of components which are included in structure of concrete and radionuclides too. This factor may be important when the cemented objects are stored without weather protection in climatic conditions in which in winter period the probably long-lived temperature fall is lower $-18-20^{\circ}\text{C}$. Such situation is represented rather improbable. Besides the conducted special researches have shown that designed cement mixtures have the class of frost

resistance not below $F=300$ according to GOST 10060-87 that guarantees preservation of properties of concrete on predictable period.

Thus as the main factor determining durability of concrete, used for conservation of radiation-hazardous objects, including waste tanks, and for solidification of the liquid radwastes, it is necessary to consider interaction of concretes with groundwater.

As a parameter of properties of concrete at estimation of their durability was chosen their compression strength because the change of this parameter mirrors changes happening in structure of concrete.

Corrosion of the cured cement mixtures at interaction with groundwater.

At contact of the cured cement mixtures with groundwater the leaching of Ca(OH)_2 takes place, rate of which is limited by Ca^{+2} diffusion through system of matrix - pores of cement mixture.

For estimation of service time of the cured mixtures on the basis of cement it is necessary to have the information on leaching rate of calcium from it. The data on leaching rate of calcium from mixtures No 2 and 21 are shown in the table 2.2.7.

Table 2.2.7.

Leaching rate of calcium from mixtures No 2 and 21.

| No of composition | Time of leaching, days | Total fraction of leached Ca(OH)_2 |
|-------------------|------------------------|--|
| 2 | 3 | 0.0144 |
| | 6 | 0.0203 |
| | 10 | 0.00263 |
| | 20 | 0.00371 |
| | 30 | 0.00456 |
| | 40 | 0.00526 |
| | 50 | 0.00589 |
| 21 | 60 | 0.00645 |
| | 3 | 0.000181 |
| | 6 | 0.000235 |
| | 10 | 0.00033 |

| | | |
|--|----|----------|
| | 20 | 0.000465 |
| | 30 | 0.000572 |
| | 40 | 0.00066 |
| | 50 | 0.000738 |
| | 60 | 0.00081 |

The diffusion coefficients of calcium in mixtures No 2 and 21, calculated on the basis of the data of table 2.2.7. are equal:

For mixture No 2 - $3.1 \cdot 10^{-15} \text{ m}^2/\text{sec}$;

For mixture No 21 - $3.8 \cdot 10^{-16} \text{ m}^2/\text{sec}$

These values of a diffusion coefficients of calcium in mixtures No 2 and 21 were used for estimation of service time of these mixtures at a contact with groundwater.

. For calculation of speed of leaching C_a it is accepted:

- the package with the cemented radwaste has the form of barrels with diameter 1 m which are located in storage as a dense packing thus the volume of groundwater directly interacting with composition is equal to $0.215 \text{ m}^3/\text{m}^3$ of cement mixture;
- the leaching rate of C_a depends on speed of groundwater current in storage therefore calculations were made for three speeds of water current : 1, 10, and 100 m / years;
- for calculation of Ca leaching rate it was adopted the model, according to which the cylindrical units of cement mixtures are completely filled up with groundwater, which is contacting with mixture definite time dependent on speed of water current in storage then it is substituted on a fresh portion of groundwater and the procedure repeats;
- the concentration of C_a in groundwater is small in comparison with it concentration in pores of cement mixture that corresponds to maximum rate of Ca leaching from mixture.

The solution of a diffusion equation for this case are known (25). In the table 2.2.8. service time of mixtures No 2 and 21 calculated on the basis of above presented reasons are shown.

Table 2.2.8.

Calculated service time of compositions N 2 and 21 at different speeds of water current in storage of cemented radwaste .
(The packages of cemented radwaste have the form of barrels with diameter 1 m).

| No of composition | Speed of water current , m / year | Service time of composition, years |
|-------------------|--------------------------------------|---------------------------------------|
| 2 | 1 | $2.5 \cdot 10^3$ |
| | 10 | $7.9 \cdot 10^2$ |
| | 100 | $2.5 \cdot 10^2$ |
| 21 | 1 | $7.0 \cdot 10^3$ |
| | 10 | $2.2 \cdot 10^3$ |
| | 100 | $7.0 \cdot 10^2$ |

As it is visible from the table 2.2.8., estimated service time of composition N 2 at speed of groundwater current in storage of radwastes up to 10 m / years will exceed demanded value 500 years, however at more high speed of groundwater in storage it stability to calcium leaching can be not enough to guarantee safe storage of the cemented radwastes on given term. Considerably best parameters has the composition No 21 for which even at speed of groundwater current 100 m / years calculated service time is 700 years, that notably exceeds time (500 years) of radwastes storage containing Cs-137 and Sr-90, demanded for practically full decay of these radionuclides.

Research of cementation of simulated radioactive pulps on MCC.

The researches on usage of cementation for solidification of radioactive pulps was made on Mining-Chemical-Combine. The portland cement M 400 was used in these researches. Permissible quantity of pulps entered in cement mixture is determined, which allows to obtain the cured cement grout corresponding to the Russian requirements (RD 9510497-93 "Quality of compounds, obtained at cementation of low and middle active liquid radioactive wastes. Specifications. MINATOM of Russian Federation, 1993).

The Main results of carried out researches are presented below.

In the table 2.2.9 the data on influence of quantity of the pulp entered into cement mixture on strength of cured mixture are shown. 10 % of bentonite from weight of cement was entered into cement mixture as the component for decreasing of leaching rates of radionuclides from cured cement mixtures..

The table 2.2.9
Influencing of quantity of pulp on strength of cured cement mixtures.

| Cement / Bentonite ratio | Composition of cement mixture. The contents, % weight. | | Weight water/ cement ratio | Compressive Strength, MPa |
|--------------------------------|---|------|-------------------------------|---------------------------------|
| | Cement + Bentonite | Pulp | | |
| 10: 0 | 100 | 0 | 0.7 | 18.0 |
| 9: 1 | 100 | 0 | 1.0 | 14.5 |
| 9: 1 | 90 | 10 | 1.0 | 17.0 |
| 9: 1 | 80 | 20 | 1.0 | 18.0 |
| 9: 1 | 70 | 30 | 1.0 | 13.0 |
| 9: 1 | 60 | 40 | 1.0 | 3.0 |
| 9: 1 | 20 | 80 | 1.0 | 1.0 |

The data, showed in the table 1, demonstrate that satisfactory compression strength, equal to 13 MPa, have samples of cured cement mixtures containing up to 30 % weight of pulp. Increasing of content of pulp in cement mixture above this limit leads to sharp decreasing of compressive strength and these mixtures does not fulfil conditions of the Russian standards of safety (RD 9510497-93).

The conducted researches have allowed to recommend for solidification of radioactive pulps the following composition of cement mixture:

- binding – portland cement M400;
- bentonite - 10 % from weight of cement;
- radioactive pulp - about 30 % from weight of cement;
- water/cement ratio 1: 1.

The leaching rate of Cs-137 and Pu-239 was studied for cement mixtures, compositions of which are shown in the table 2.2.10

The table 2.2.10

Composition of cement mixtures for research of leaching rate of Cs-137 and Pu-239.

| N Of sam ple | Composition of cement mixtures, weight % | | | | | | Activity Ci/kg |
|-----------------------|--|----------------|---------------------|-----------------------|---------------------------|-------------------|----------------------|
| | Cem- ent | Bento- nite | Clino- ptilolite | Rad- waste pulp | Water/ cement ratio | Radio- nuclide | |
| 1 | 100 | - | - | 35 | 1.0 | Cs-137 | 2.0x10 ⁻³ |
| 2 | 90 | 10 | - | 33 | 1.1 | Cs-137 | 1.8x10 ⁻³ |
| 3 | 95 | 5 | - | 34 | 1.1 | Cs-137 | 1.9x10 ⁻³ |
| 4* | 91 | 9 | - | 33 | 1.0 | Cs-137 | 1.8x10 ⁻³ |
| 5 | 91 | - | 9 | 33 | 1.0 | Cs-137 | 1.8x10 ⁻³ |
| 6 | 100 | - | - | 35 | 1.0 | Pu-239 | 1.3x10 ⁻² |
| 7 | 91 | 9 | - | 33 | 1.1 | Pu-239 | 1.3x10 ⁻² |
| 8* | 91 | 9 | - | 33 | 1.0 | Pu-239 | 1.2x10 ⁻² |

The notice - * in samples 4 and 8 the bentonite dried up to constant weight at temperature 100 °C was added.

The data on leaching rate of Cs-137 and Pu-239 from investigated cement mixtures are presented in the tables 2.2.11 and 2.2.12.

The table 2.2.11.

Leaching rate of Cs-137 from cement mixtures (composition of samples presented in table 2.2.10).

| Contact time of sample with water, days. | Leaching rate of Cs-137 from samples of cement mixtures, g/sm ² xday | | | | |
|--|---|----------------------|----------------------|----------------------|----------------------|
| | 1 | 2 | 3 | 4 | 5 |
| 15 | 8.5×10^{-3} | 1.3×10^{-3} | 3.1×10^{-3} | 1.6×10^{-4} | 1.6×10^{-3} |
| 28 | 5.1×10^{-3} | 8.8×10^{-4} | 1.8×10^{-3} | 8.0×10^{-5} | 5.0×10^{-4} |
| 58 | 2.6×10^{-3} | 4.1×10^{-4} | 8.2×10^{-4} | 3.0×10^{-5} | - |
| 150 | 2.0×10^{-3} | 8.5×10^{-4} | 3.8×10^{-4} | 8.0×10^{-5} | - |
| 190 | 1.0×10^{-3} | 1.3×10^{-4} | - | 2.5×10^{-5} | - |
| 265 | 1.0×10^{-3} | 1.0×10^{-4} | - | 1.0×10^{-5} | - |
| 350 | 1.0×10^{-3} | - | - | - | - |

The table 2.2.12

Rate of Pu-239 leaching from cement mixtures

(composition of samples presented in table 2.2.10).

| Contact time of sample with water, days. | Rate of Pu—239 leaching from samples of cement mixtures, g/sm ² xday. | | |
|--|--|----------------------|----------------------|
| | 6 | 7 | 8 |
| 15 | 9.2×10^{-5} | 3.3×10^{-5} | 1.0×10^{-5} |
| 48 | 2.1×10^{-5} | 1.0×10^{-5} | 4.0×10^{-7} |
| 140 | 2.0×10^{-7} | 2.0×10^{-7} | 1.0×10^{-7} |

The results of the carried out experiments have shown that the addition of clinoptilolite and bentonite, especially bentonite dried up to constant weight at 100 °C, essentially decreases leaching rate of Cs-137 from cement mixtures. In case of plutonium the influencing of bentonite addition on leaching rate is not so significant.

The experiments, results of which presented above, were carried out without exchange of contact solution that imitated emergency submergence of radwastes storage.

Magnesium-phosphate cement for solidification of the liquid radwastes and pulps directly in waste tanks.

In a number of cases there is a necessity of solidification of the liquid radwastes or radioactive pulps directly in waste tanks in which the stirring is very difficult or is impossible. The carried out researches have shown that for this purpose it is perspective to use cements on the phosphate basis which is forming at interaction of phosphoric acid with compounds of different metals, in particular with caustic magnesite.

In work /27/ the main positions reflecting influence of chemical composition of phosphate compounds on capability and on conditions of development of astringent properties were formulated:

1. The phosphate cements are received at interaction of phosphoric acid with powdery materials (oxides, hydroxides, phosphates etc.) in broad range of their composition.
2. The intensity of development of astringent properties in system " oxide - phosphoric acid " is objective function of value of ionic potential (relation of a charge to effective radius) cation of oxide.
3. The major factor determining a capability of obtaining of phosphate cement is the right selection of ratio of reaction rate of phosphoric acid with oxide (generation rate of germs of crystals) and speed of gelation of cement.

Application of cements of phosphate solidification for an immobilization of radioactive waste is perspective from the point of view of strong fixation of radionuclides in structure of cement mixture. The large group of mineral ion exchangers is known on the basis of indissoluble salts of phosphoric acids

/28/, such as phosphates of barium, tin, zirconium, thorium etc., which effectively retain different radionuclides. It gives the basis to guess that after immobilization of radioactive waste in phosphate cement there will be a strong fixation of radionuclides.

On the basis of above-stated it was offered technique /28/ of solidification of liquid radioactive wastes with applying as binding of magnesium-phosphate cement.

In according to this technique in radioactive waste the concentrated orthophosphoric acid and caustic magnesite must be sequentially added at weight ratio radwaste pulp: orthophosphoric acid: caustic magnesite equal to 1:0,3:0,5 accordingly. After that the mixture is maintained during time which is necessary for solidification. The plant tests /30/ on solidification of 70 m³ of radioactive ferrocyanide pulp directly in defective radwaste storage tank - AG - 8301/1 having volume 3200 m³ at radiochemical plant MCC was made. On technological calculations for solidification of 70 m³ of pulp having ratio solid to liquid phase equal 1:2, it was required 25,8 t of concentrated phosphoric acid and 42 t of caustic magnesite. The distinctive feature of technological process of solidification was that in the tank the system of mixing was absent that complicated process of solidification. As a result of it, after supply in the tank of all quantity of phosphoric acid and the first portion (3,5 tons) of caustic magnesite the dense layer of magnesium-phosphate cement was formed on the surface of pulp that precluded entry of caustic magnesite into mixture of pulp and phosphoric acid and because of that has not given capability to finish process of solidification.

In laboratory conditions the researches were carried out to choice the conditions of the introducing in waste tank of phosphoric acid and caustic magnesite which would give a capability to make solidification in all volume of waste. The results of these experiments show that for this purpose it is necessary:

- concentration of phosphoric acid in waste must be 90-106 g/l;
- all demanded quantity of caustic magnesite should be entered in one portion during possible short time;
- after the addition of magnesite the system must be stayed during 100 day for solidification of the formed cement.

In accordance with recommendations prepared on the basis of results of laboratory researches, the following technological decisions were adopted:

- to add in tank calculated quantity of water for decreasing of density of aqueous phase of pulp from 1.412 g/sm³ to 1.32 g/sm³ and decreasing of phosphoric acid concentration from 196 g/l up to 106 g/l;
- the addition of all demanded quantity of magnesite carry out in one portion during possible short time;
- after magnesite addition to add in tank 1.5 t of phosphoric acid to guarantee obtaining of magnesium-phosphate cement on the surface of waste.

After carrying out of all these operations reaction mixture in tank was stored during 100 days. The samples, which were taken after that, showed that magnesium-phosphate cement monolith was formed in whole volume of radwaste in tank.

The carried out works have allowed to solidificate 70 m³ of radioactive pulp that gave possibility to localize radionuclides in cured cement mixture and to eliminate leakage of radionuclides from defective tank in ground waters.

The installations for cementation of radioactive wastes developed in Russian Federation.

The method of cementation is considered in Russian Federation now as the main method for reprocessing of low and middle active radwastes. In this connection the significant attention in Russia was paid to developing of equipment for this purpose

To the present time the number of such installations is designed, the brief description and the characteristics of which are presented below.

1. Installation of cementation on RTP "ATOMFLOT".

The installation is designed for cementation of radioactive wastes which are obtained at exploitation of atomic -powered icebreakers.

The radwastes of different chemical and phase composition can be processed on this installation:

- saline solutions including brines and concentrate from the installation of membrane cleaning;

- hydroxide pulps;
- pulps of inorganic sorbents.

Cement mixtures obtained on the installation, are packaged in protective concrete containers UNZK-150-1.5P with capacity 1.5 m³. Activity of cement mixtures must be not more than 6×10^{-3} Ci/kg.

Structure of the installation.

The installation consists of five blocks:

- system of cement feed in the block of mixture preparation;
- system of radwastes preparing and its feed in the block of cement mixture preparation;
- block of cement mixtures preparation and discharging of it in the container;
- system of containers transportation;
- the control system.

Characteristics of the installation.

| | | |
|-----|---|--------------------------|
| 1. | Concentration of salts in radwaste solutions, g/l | Up to 200 |
| 2. | pH of solutions | 7 - 10 |
| 3. | Specific activity of solution, Bq/l | Up to 1.86×10^7 |
| 4. | Concentration of solid phase in pulp, g/l | Up to 200 |
| 5. | Specific activity of pulp, Bq/l | Up to 2.22×10^8 |
| 6. | Consumption of cement, kg/hour | 600-1200 |
| 7. | Consumption of the additions, kg/hour | 60-120 |
| 8. | Consumption of compressed air (6 atm.), kg/hour | Up to 50 |
| 9. | Yield of waste gases, kg/hour | Up to 60 |
| 10. | Specific activity of overflow gases, Bq/m ³ | Not more than 3.7 |
| 11. | Weight water-cement ratio | 0.4-0.7 |
| 12. | Weight fraction of salts in cement mixture, % | Not less than 7 |
| 13. | Weight fraction of pulps solid phase in cement mixture, % | 7-8.5 |
| 14. | Degree of the container filling, % | Not less than 85 |
| 15. | Consumed electrical power | No more than 32.5 kw |
| 16. | Temperature of air at exploitation | 5 – 40 °C |

2. Installation for cementation of the ash from incineration of combustible solid radwastes on Smolensk Nuclear Power Plant..

The installation of cementation is designed for cementation of the ash which is obtained at incineration of solid combustible radioactive wastes. It

contains up to 99 % of radionuclides from their quantity in an initial combustible solid radioactive waste.

The installation includes:

- bunker for cement;
- vessel for water;
- vessel for collecting of ash with volume 200 l;
- the automotive protective container;
- auger feeder for ash;
- feeder for batching of cement;
- unit for mixing of ash, cement and water.

Characteristics of the installation.

Filled with ash the barrel located in the automotive protective container, goes on the installation of cementation.. The barrel with ash is connected to the cover having the electric drive with mixer and admissions for cement and water.

The cement feeds from bunker with portions up to 70 kg.

The water feeds from vessel with portions up to 70 l.

The consumption of cement - 0.6 - 1.0 kg / hour.

Quantity of cement compound - 1.6 - 2.6 kg / hour.

Specific activity of cement compound - up to 1×10^{-2} Ci/kg.

3. Installation of cementation liquid radwastes in building 101

NITI.

The installation is designed for cementation of liquid radwaste concentrates. The solidification is made directly inside primary packaging (barrel).

The installation can be utilized on objects, on which the volume and regularity of liquid radwastes formation make stationary installation economically inexpedient.

The portland cement M500 (GOST 10178-85) will be used for cementation of liquid radwaste concentrates. The different synthetic and natural inorganic sorbents (nickel ferrocyanide on silicogel (NGA- "Celeks - CFN" TU 95-2385-92, bentonite clay (GOST 7032-75), clinoptilolite,

vermiculite etc.) in quantity 5-15 % from weight of cement can be applied as sorbing additives.

The modular design is adopted for installation that allows to convey it on different objects.

Characteristics of the installation.

| | | |
|-----|---|--|
| 1. | Installation capacity: - on concentrate of liquid radwastes , m ³ /year - on cement compound, m ³ /year: | 100 Up to 142 |
| 2. | Concentration of salts in radwaste solutions, g/l | Up to 200 |
| 3. | Quantity of components on cementation of one barrel: - concentrate of liquid radwastes , l - cement, kg - sorbing components, kg | 126 180 10 |
| 4. | Weight of barrel with cement compound, kg | Up to 350 |
| 5. | Specific weight of cement compound, kg / l | 1.8-2.0 |
| 6. | Volume of barrel with cement compound, l | 200 |
| 7. | Radiochemical composition of liquid radwastes | Co-60, Sr-90, Cs-137 |
| 8. | Average chemical composition of liquid radwaste concentrates : HCO ₃ Cl- SO ₄ -2 NO ₃ - Ca+2 Mg+2 Na + K + NH ₄ + Fe+3 Petroleum PH Density, g/l | 25-35 % 18-25 % 10-15 % 1-2 % 8-12 % 1-5 % 8-12 % 4-8 % 0.1-0.3 % 1-3 % 1.5 %? 6.5-8.5 1.045 |
| 9. | Specific activity of liquid radwastes concentrate , Ci/l | 1x10 ⁻⁵ |
| 10. | Consumed electrical power, kw | Up to 5 |
| 11. | Operational mode of the installation | Periodic |
| 12. | The design of installation | Modular |
| 13. | Quantity of modules at transportation | 2 |
| 14. | Overall dimensions, mm Module 1 Module 2 | 3500x1350x2000 3500x2600x2000 |
| 15. | Weight of the installation (net), kg Module 1 Module 2 | 1000 2000 |

4. Installation for cementation radwastes on Moscow NPO "Radon".

The modular installation of cementation with the vortex mixer designed for processing of liquid radwastes concentrates, pulp of ion-exchange resins and inorganic sorbents.

Cement compound obtained on the installation with activity not more than 5×10^{-4} Ci/kg is packaging in steel barrels with volume 200 l.

The installation consists of following modules:

- preparation of cement mixture;
- transport;
- preparation of pulps;
- preparation of inorganic sorbents ;
- preparation of ionexchange resins;
- pumps-batchers;
- ventilation;
- control panel;
- electric switchboard.

Characteristics of the installation.

| | | |
|-----|--|---------------------------------------|
| 1. | Capacity on cement grout, m ³ /hour | 1.5 |
| 2. | Capacity on liquid radwastes (at (water/cement ratio – 0.75), m ³ /hour | 1.0 |
| 3. | Concentration of salts in radwaste concentrates , g/l | Up to 1000 |
| 4. | Cementing material | Portland cement M400 and M500 |
| 5. | Density of cement grout, kg / l | 1.5-2.2 |
| 6. | Rate of Cs-137 leaching, g/ sm ² xday | $2 \times 10^{-3} - 4 \times 10^{-5}$ |
| 7. | The sorbing additives | Bentonite, natural zeolites |
| 8. | Quantity of the sorbing additives, % of weight of cement grout | 1 – 5 % |
| 9. | Quantity of superplasticizer, % of weight of cement grout | 0.1 – 1.0 % |
| 10. | Water/cement ratio | 0.4 - 0.8 |
| 11. | Specific activity of reprocessed solutions, Ci/l | Up to 1×10^{-3} |
| 12. | Operational mode | Periodic or continuous |
| 13. | Process control | Manual or automatic |
| 14. | Primary packaging | Steel barrel V=200 l |

| | | |
|-----|---|------------------|
| 15. | Service life of the installation, years | Not less than 10 |
| 16. | Total mass, metric ton | 27 |
| 17. | Consumed electrical power, kw | 150 |

The modular installation of cementation with the vortex mixer provides high quality of cement grout, has capability of fast change of its structure depending on kind of reprocessed radioactive waste, allows to reprocess waste with the considerable contents of solid suspended matters and enables to lower quantity of secondary waste (decontamination water used for washing of the mixing chamber).

5. Installation of cementation of liquid radioactive waste "ATOMmash".

The modular installation of cementation is designed for solidification of concentrates obtained at evaporation of liquid radwastes, pulps of filtering materials and liquid organic waste of low activity level.

Cement grout with specific activity no more than 1×10^{-4} Ci/kg obtained on the installation is packaged in steel barrels with volume 200 l.

Characteristics of the installation.

| | | |
|-----|--|-------------------------------|
| 1. | Capacity on cement grout, m ³ /hour | 1.0 |
| 3. | Concentration of salts in radwaste concentrates, g/l | Up to 200 |
| 4. | Cementing material | Portland cement M400 and M500 |
| 5. | Density of cement grout, kg / l | 1.5-2.2 |
| 6. | The sorbing additives | Bentonite, natural zeolites |
| 7. | Quantity of the sorbing additives, % of weight of cement grout | 1 – 5 % |
| 8. | Quantity of superplasticizer, % of weight of cement grout | 0.1 – 1.0 % |
| 9. | Water/cement ratio | 0.4 - 0.8 |
| 10. | Specific activity of reprocessed solutions, Ci/l | Up to 5×10^{-4} |
| 11. | Operational mode | Periodic or continuous |
| 12. | Process control | Manual or automatic |
| 13. | Primary packaging | Steel barrel V=200 l |

In conclusion the basic characteristics of the installations of cementation designed in Russia are presented below.

Basic characteristics of the Russian installations of cementation.

| The characteristics of the installations | Place of location of the installation | | | | |
|--|---|--|--|--|--|
| | RTP "ATOMFLOT" | Smolensk NPP | RNC "NITI" | Moscow SPA "RADON" | ATOMmash |
| Composition of the cemented radwastes | Liquid radwastes with salt content up to 200 g/l, hydroxide pulps and pulps of inorganic sorbents | Ash from incineration of combustible solid radwastes. | Liquid radwastes with salt content up to 200 g/l, pulp of ion-exchange resins and inorganic sorbents | Liquid radwastes with salt content up to 1000 g/l, pulps of ion-exchange resins and inorganic sorbents | Residues from evaporation of liquid radwastes, pulps of filtrating materials, liquid organic Low level radwastes |
| Capacity on cement – grout | Up to 1.0 m ³ /hour | Up to 2.6 Kg / hour | Till 0.13 m ³ /hour | Up to 1.5 m ³ /hour | Up to 1.3 m ³ /hour |
| Specific activity of cement grout, Ci/kg | Up to 6x10 ⁻³ | Up to 1.0x10 ⁻² | Up to 1.0x10 ⁻⁵ | Up to 5x10 ⁻⁴ | Up to 4x10 ⁻⁴ |
| Type of cement grout package | The protective concrete container UNZK-150-1.5P | Steel barrel V=200 l | Steel barrel V=200 l | Steel barrel V=200 l | Steel barrel V=200 l |
| Design features of the installation | Fixed location in building with radiation protection. | Fixed location in building with radiation protection. | The modular installation | The modular installation | The modular installation |
| Development stage | Installation is mounted on RTP "ATOMFLOT" and now is in industrial testing | The working documentation is designed and confirmed by regulatory authorities. | The cold tests of experimental Installation was carried out | Installation is mounted on Moscow NPO "RADON" and now is in industrial exploitation | The working documentation is designed and confirmed by regulatory authorities. |
| Enterprise-Designer | SverdNIlchim - mash | GI VNIPIET | RNC "NITI" | Moscow NPO "RADON" | "ATOMMASH" |

3. LARGE SCALE EXPERIENCE OF APPLICATION OF CEMENTATION METHODS FOR CONSERVATION OF RADIATION-HAZARDOUS OBJECTS IN RUSSIA.

Up to the present time in Russia there is no experience on applying of cementation for conservation (closure) of waste tanks. It is connected with that waste tanks in which the main part of the accumulated radwastes is

stored in Russia manufactured from corrosion-resistant stainless steel that reduces to minimum hazard of affect of these wastes on environment.

The radiation-hazardous objects of nuclear fleet removed from exploitation have significantly larger hazard to environment therefore on conservation of these objects it is paid prime attention now.

To the present time the large scale works on conservation of two objects of nuclear fleet were made:

- floating technical base "Lepse" (ship assigned to maintenance of atomic ice breakers) of Murmansk marine shipping company;
- two reactor compartments of nuclear submarines in former training center of the Russian Navy in Paldisk, Estonia.

1. Cementation of intertank space of burned up fuels storage on "Lepse".

For adjustment of radiation conditions on "Lepse" in accordance with the present Russian standards in 1990 it was accepted the decision to fill in intertank space of burned up fuels storage on this ship with concrete - conserving agent.

The monolith formed by concrete - conserving agent should become an engineering barrier ensuring increase of strength of all construction and also as immobilization barrier to prevent possible migration of radionuclides from burned up fuels storage in environment.

1.1. Design of intertank space of burned up fuels storage on «Lepse».

The burned up fuels storage on "Lepse" represents located in the nose of the ship rectangular compartment with metallic walls inside of which there are placed two cylindrical tanks with burned up fuel assemblies. Assemblies are placed in capsules arranged by concentric series and intercapsule space is filled by water serving for cooling of capsules. The water circulation is provided with special system. The tanks are closed by rotary covers permitting selectively to open access to capsule and assembly which must be overload.

Burned up assemblies storage has the internal sizes 4800x10150 mm and walls with thickness 420 -450 mm. The tanks having diameter 3600 mm and height 3440 mm are made from stainless steel with thickness 10 mm.

For creation of engineering barrier in intertank space it was necessary to fill it with 102 m³ of cement mixture. It was made with the purpose of strengthening of storage in view of possible accidents at all technological stages of the management of burned up assemblies and at long-term storage in repository.

1.2. General requirements to materials of engineering and immobilization barriers.

To the cured cement mixtures:

- to provide protection of metallic constructions of burned up assemblies storage from corrosion under affect of the external factors; do not accelerate and do not instigate corrosion of available protective contours of storage;
- to be steady against long-lived radiation effect;
- to have high durability, the value of compressive strength of concrete - conserving agent at the end of calculated storage time (500 years) should be not less than 100 kg /cm² (10 MPa);
- to be non-toxic, flame safety and fireproof.

The mixtures prepared for conservation of radiation-hazardous objects must:

- to have flow characteristics indispensable for full filling of space of the complex configuration;
- the used mixtures should be not toxic, are explosion-proof and fireproof;
- mixtures and their rheological characteristics should provide a capability of their mechanical preparation, transport, supply and stacking with usage of equipment serially produced and used in building;
- the materials should be not deficient

1.3. General requirements to technology of conservation of the object:

- the technology of object filling with cement mixtures should be completely mechanized and remotely operated;
- the technological circuit for object cementation should be highly reliable;
- mounting of the part of technological circuit for packing of mixtures in radiation-dangerous zone and process of packing of mixtures should requires of minimum workers participation at carrying out of all requirements and standards of radiation safety.

1.4. Materials and technology for cementation of intertank space.

In accordance with data of radiation safety service of Murmansk marine shipping company the integral radiation dose of concrete in intertank space of burned up assemblies storage for estimated time of storage of "Lepse" will not exceed 1×10^8 rad. Thus for this object it is not required applying of special highly radiation stable concrete. Outgoing from this for filling of intertank space on "Lepse" the concrete on the basis of portland cement and customary fillers (sand, Breakstone) satisfying to GOST 10260-80 was selected. Such concrete mixtures also fit to all, formulated above, requirements: they are not toxic, are fire- and explosion-proof, the materials to their preparation are accessible and mixtures preparation, transport, supply and stacking can be made with usage of serially produced and widely applicable in building equipment.

Due to modern achievements of concrete technology, it is possible to receive not stratified homogeneous mixtures possessing high fluidity, capable to stuff completely internal volumes of objects of the complex configuration.

At the same time, it, as a rule, demands of the heightened consumption of cement. In this connection special attention was paid to limitation of mixture temperature growth during cementation and subsequent curing of concrete monolith to except thermal crackforming in concrete. On the basis of the carried out experimental works for the solution of this problem it was determined to do cementation of intertank space of burned up assemblies storage on "Lepse" in October when climatic conditions near Murmansk allow to receive concrete mixtures with temperature $5-10^{\circ}\text{C}$ without addition cooling. This measure and usage for cooling of curing concrete of cooling system of burned up fuel storage has allowed to limit temperature rise in concrete no more than $35-40^{\circ}\text{C}$ that completely eliminated hazard of dangerous thermal stresses in concrete monolith.

For cementation of intertank space on "Lepse" the concrete mixture on the basis of low aluminate portland cement was used the composition of which is shown in the table 1.1.

Table 3.1.

Composition of concretes used for cementation of intertank space of burned up assemblies storage on "Lepse"

| The naming of materials, parameters of concrete mixture | Units of measurement | The consumption of materials on 1 m ³ of concrete | |
|--|-------------------------|--|-----------|
| | | | |
| Portland cement: | | | |
| of the mark: "400" | Kg | 415 | - |
| "500" | Kg | - | 380 |
| Sand | Kg | 650 | 740 |
| Breakstone (size up to 20 mm) | Kg | 975 | 1020 |
| Water : cement ratio | | 0,48÷0,5 | 0,42÷0,45 |
| Additives: | | | |
| Superplasticizer | | S-3 | S-3 |

Concrete mixtures were prepared on usual concrete plant and transportation of concrete to "Lepse" was made with help of automobile concrete mixers.

The system consisting of the "Wartington" concrete pump and concrete line connected the pump placed on a coast with a receiving hutch on "Lepse" was used for stacking of concrete. In total in intertank space was pumped 110 m³ of concrete, on what it was required about 6 hours.

The check tests have shown that the concrete monolith has no defects, the compression strength of check samples of concrete in the age of 28 day was equal to 27.6 mPa. Thus it is possible to draw a conclusion, that the conservation of burned up assemblies storage on "Lepse" has passed successfully.

2. Decommissioning and preparing to safe storage during 50 years of reactor compartments nuclear submarines in training center of Russian Navy in Paldisk Estonian Republic.

Training center of the USSR Navy in Paldisk was put into exploitation in 1967. There were two real reactor compartments of nuclear submarines and necessary power equipment, (steam generators, turbines etc.). The nuclear power plants in training center were working up to 1989.

After finding by Estonia of the status of the independent state it was raised the question about liquidation of training center of Russian Navy in Paldisk. In accordance with intergovernmental Agreement between Russia and Estonian Republic nuclear objects of training center must be decommissioned and prepared to long-term (50 years) safe storage till 30 September, 1995.

In accordance with this agreement it was carried out complex of works including:

- comprehensive engineering inspection of the objects;
- elaboration and adjustment of the concept of decommissioning and preparation to safe storage of nuclear objects of training center;
- elaboration of the project documentation for carrying out of the works and technology of cementation of reactor compartments and other systems of nuclear power plants;
- hermetic sealing of reactor compartments;
- conservation of reactors, equipment and systems of nuclear power plants;
- building of protective shelters (sarcophagi).

The complex of buildings and facilities of a training center provided realization of all technological operations indispensable for exploitation of reactors and other systems of nuclear power plants in conditions maximum approximated to real.

At exploitation of the installations the carrying out of the following operations was required:

- storage and audit of fresh fuel assemblies, rods of management and protective system etc.;

- recharge of active zones of the reactors;
- replacement of separate components of reactors and equipment of the steam generating installations;
- cooling of the burned up fuel assemblies;
- cooling of radioactive components of reactors and equipment of steam generating installations;
- loading of cooled burned up fuel assemblies on an external transport;
- disposal of the radioactive equipment.

The systems of training center provided carrying out of all these operations.

2.1. Comprehensive engineering inspection of the nuclear objects of the Navy training center.

Comprehensive engineering inspection of nuclear objects of the Navy training center was made to obtain the data necessary for designing of technology and documentation for decommissioning of these objects. The inspection was conducted in two stages. The first stage was done in January, 1994 for elaboration of the concept of decommissioning of nuclear objects and second stage was made after discharge of nuclear fuel from reactors and disposal of liquid and gaseous mediums from systems and equipment to obtain the indispensable additional data for designing technology of objects conservation and preparing of project-budget documentation.

Engineering inspection included:

- estimation of actual condition of buildings, equipment and systems of reactor compartments and other equipment of nuclear power plants;
- itemization of the design and technological solutions on equipment and systems disassembly and their preparing to conservation and long-term storage;
- full-scale measurements of overall dimensions of a reactor compartments necessary for designing of protective shelters;
- radiation examination of reactor compartments, buildings and territory.

On the base of results of engineering inspection the following conclusions were made:

- the dose rate of γ -radiation on territory of training center is equal to 16 -

23 μ R/h and corresponds to background values for the given terrain;

- technical condition of buildings and equipment is satisfactory;
- the radiation examination has shown, that in all placement, excepting reactor compartments, there is no excess of background values β^- and γ^- activity;
- γ^- radiation dose rate in reactor compartments is equal to 0,1 - 23 mR/h.

The obtained results of engineering examination have allowed to accept the optimal and economically reasonable solutions at elaboration of technology and project documentation.

2.2. The concept of decommissioning and preparation to safe storage of nuclear objects of training center

The modern concepts of decommissioning and preparation for long-term storage of nuclear objects envisage their deep decontamination and disassembly, including constructions with induced radiation. The realization of the similar concepts is connected with formation big quantity of highly active solid radioactive wastes and secondary liquid radioactive wastes. Processing and solidification of these wastes are very complex, expensive and long-timed processes requiring of creation of new productions.

In conditions of a nuclear training center in Paldisk the indicated concept could not be used because of very short period of time which was given on all works (nuclear objects of training center must be delivered to Estonian party till September, 1995) and also because of the limited financial capabilities of Russian party. All this dictated necessity of acceptance of new more optimal solutions.

In view of IAEA principles of safety and technical criterions for underground disposal of the radioactive wastes (serial of issues on safety, No 99, Vienna 1990, the section 3 "Principles of safety") was necessary to find a solution answering to the following requirements:

- providing of safety ;
- liability before the future generations;
- consequences in the future: " It is necessary to ensure a degree of isolation of highly radioactive wastes at such level that there were absent predictable kinds of risk for people health or consequence for an

environment in the future, which would not be acceptable today".

For carrying out of the indicated conditions and requirements, on fifty years period of reactor compartments storage in accordance with really existing radiation situation, it was necessary to create a number of engineering barriers precluding migration of radionuclides in environment and eliminating unauthorized admittance of the people into reactor compartments.

The following system of reactor compartments preparation to long-term storage was adopted to realization:

- preparing of devices and systems of reactor compartments and steam generating installation to conservation with the help of concrete - conserving agents;
- creation immobilizing and engineering barriers inside reactor compartments;
- building protective sarcophagi outside of reactor compartments designed for protection of reactor compartments from extreme impacts natural and technical origin within 50 years.

The preparation of devices and submarine inner compartments and of steam generating installation to constitutes barriers for disassembly and deleting of the uncontaminated equipment was done prior to sealing reactor compartments. The hermetic sealing involved plugging pipe lines, holes in body of reactor compartments with grout prior to the compartment test on air-tightness. Besides these works dehumidifying of air inside reactor compartments and deposition of outside protective coatings on bodies of compartments were made.

In result of engineering inspection the list of equipment and devices of reactor compartments must be conserved with help of special concrete mixtures was determined.

On the basis of results of researches of properties of special portland cement mixtures, presented in this review, for conservation of reactor compartments the mixture No 2 was selected, in which as the main components of mixture except of cement will be used finely divided shungizit and shungizit sand. For giving high fluidity to concrete mixture in it the superplasticizer S-3 was added, and for increase of concrete gas permeability the component SDO was introduced.

The composition of concrete, which were used for conservation of reactor compartments and the creation of external shelters (sarcophagi) are shown below.

Composition of concrete mixture No 2 for conservation of reactor compartments (consumption of materials on 1 m³ of concrete):

| | |
|--|----------|
| Portland cement of Pikalev plant M 500 | - 726 kg |
| Shungizit filling material | - 259 kg |
| Shungizit sand | - 621 kg |
| Water | - 372 kg |
| Superplasticizer S-3 | - 5.4 kg |
| SDO | - 0.4 kg |

Mean density of concrete of 2000 kg / m³

For building external shelters the concrete of the following composition was used (consumption of materials on 1 m³ of concrete):

| | |
|---|----------|
| Portland cement of Pikalev plant of M 400 | - 400 kg |
| Sand - | - 512 kg |
| Breakstone (fraction no more than 10 mm) | - 836 kg |
| Water | - 246 kg |
| Superplasticizer S-3 | - 6.0 kg |

Mean density of concrete of 2000 kg / m³.

All activities on conservation of the equipment of reactor compartments and building of external shelters were finished to the end of September, 1995 and were adopted by the Estonian party which stated that the carried out works guaranteed safety of decommissioned reactor compartments on demanded period (50 years).

CONCLUSION.

The results of done researches have shown that the composition of portland cement mixtures has high influence on properties of these mixtures. Changing composition of cement mixtures it is possible to obtain mixtures possessing complex of properties in the most degree adequate to areas of their applying.

In the present review we considered two fields of application of portland cement mixtures:

- conservation (closure) of radiation - hazardous objects of atomic engineering, in particular of waste tanks, reactor compartments of vessels with nuclear energy installations etc.;
- solidification and preparing for long-term storage of the liquid radwastes.

The optimal complex of properties of cement mixtures designed for applying in each of introduced above areas can be various.

So at usage of these mixtures for conservation of radiation - hazardous objects with high-level of radiation the important value has a high gas permeability of using mixtures because that allows to ensure going out of radiolytical gases without disturbance of concrete monolith integrity. For cement mixtures intended for solidification of the liquid radwastes middle and low level of activity the requirements of low leaching rate of radionuclides and high stability of mixture at affect of groundwater and other factors of environment of radwastes storage are going on the foreground.

Considering from these positions results of researches of portland cement mixtures it is possible to make following conclusions.

For conservation (closure) of radiation-hazardous objects with high level of radiation for which the release of significant amount of radiolytical hydrogen is possible, the most favourable combination of properties has the composition No 2, as it has a high gas permeability that provides output of hydrogen from massive of the cured composition without disturbance of it integrity.

For conservation of radiation-hazardous objects with low radiation level, for which quantity of emanation of radiolytical hydrogen is insignificant, and for solidification of the liquid radwastes the preference is necessary to give to composition No 21, which has a low permeability, low rate of radionuclides leaching and highest stability to affect of groundwater from studied compositions on the basis of portland cement. Estimation of possible service time of composition No 21 showed that even in disadvantageous condition (groundwater flow in repository up to 100 m/year) durability of it must be more 500 years – the time which is necessary for practically full decay of Cs-137 and Sr-90.

The technologies of cementation of radiation-hazardous objects of nuclear fleet was elaborated with accounting of results of carried out investigation. This permitted to make up to date the large scale works on conservation with help of concrete of two objects of nuclear fleet:

- floating technical base "Lepse" (ship assigned to maintenance of atomic ice breakers) of Murmansk marine shipping company;
- two reactor compartments of nuclear submarines in former training center of the Russian Navy in Paldisk, Estonia.

In the short review it is impossible to present all results obtained in cement mixtures researches carried out in Russia. But presented results permits to formulate key technical questions that can be the matter of analytical and experimental investigations in the potential Part 2 of the project:

- elaboration of new compositions of mixtures on the base of cement and other inorganic binders for liquid radwastes solidification and for closure of tanks and other radiation-hazardous objects;
- looking for additives to cement which can strongly retain in cement matrixes the certain radionuclides (Cs-137, Sr-90, Tc-99, I-129, Np-237);
- investigation of radiation-chemical processes taking place at cement mixtures irradiation to look up of the ways of decreasing of hydrogen generation.

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